LEAD-FREE COPPER ALLOY AND A METHOD OF MANUFACTURE

FIELD OF THE INVENTION

[0001] The invention relates to a copper alloy based on Cu-Zn-Sn and a method of manufacture thereof.

BACKGROUND OF THE INVENTION

[0002] Brass is being utilized in different areas of mechanical engineering, electrical engineering and sanitation technology.

[0003] The components in mechanical engineering and in electrical engineering are becoming increasingly smaller and more filigree due to the trend toward miniaturization. Also, components of brass are often connected with other metallic and non-metallic materials to form complicated groups of components. However, both make a recycling of the materials based on a separation or division more difficult.

[0004] Further difficulties occur in particular when the components to be recycled contain toxic or health-threatening elements or substances. These can directly endanger the workers in a factory which produces and processes these materials. An environmental impact is created when such materials must be stored for a prolonged period of time and are thereby subjected to atmospheric influences. In addition, the toxic substances may contaminate the accessory agents, for example, the separating means, which are utilized during the preparation of shredder fractions via the sinking or floating method. An expensive waste disposal of the accessory agents would then be needed. Of course, health-threatening substances and elements are also undesired during the use of the components if an emission into the environment or a living organism cannot be completely avoided.

[0005] Thus, a composition which is non-threatening with respect to ecological and toxic reasons is important for such products. The increased concerns about the environment, which can be found in many standards and technical controls, for example the re-enacted drinking-water regulation DIN 50930-6 or the scrap-material regulation, demands suitable materials.

[0006] The field of electrical engineering utilizes mainly Pb-containing brass as a contact material, namely as stationary contacts or solid contacts, part of which are, for example, clamping joints and plug connectors or connector contacts. When choosing the material, its easy processing stands in the foreground. The respective componentry can be manufactured with a high degree of productivity out of a machinable Pb-containing brass.

[0007] The Pb particles in the structure create disadvantages. The particles, which act as chip breakers, however, reduce the strength or ductility of the material due to a notching tendency and reduction of the load-bearing cross-section. These disadvantages must be compensated for by suitably dimensioning the component.

[0008] All fastening elements have, caused by their manufacture, a more or less inherently high mechanical stress. These are often superposed by tensile-load tensions which are caused by screw connections. When the clamping joints are manufactured out of common Pb-containing brass, there exists, due to such tensions, a great danger for tension stress corrosion cracking.

[0009] In addition, there also exists a need for ecologically compatible materials in the field of electrical engineering. Looking at the directives given by the European Parliament regarding electrical and electronic apparatus, it can be seen that, within a reasonably short period of time into the future, Pb will

become an undesired alloy part. The goal of this initiative is, in this connection, to increase the portion of environmentally friendly materials in the material cycle.

[0010] Furthermore, components or containers for the transport or the storage of liquids are made out of Pb-containing brass. An important area is the sanitation technology. Negligence regarding the metal is especially particularly problematic here. The materials being used should thus be hardly susceptible to any type of corrosion. The components for the transport or the storing of liquids are, as a rule, manufactured by machining, often preceeded by hot forming via die-forging.

[0011] Such lead-containing brass alloys are known, for example, from the Reference DE 43 08 371 C2, which are used as a material for slide elements in cars, ships and airplanes. This alloy receives also its good machining ability from an admixture of a considerable amount of lead.

[0012] The further development of easily machinable lead-free malleable alloys based on copper is known from the Reference DE 691 24 835 T2. The alloy is supposed to replace present lead-containing materials without changing the processing conditions. Instead of lead, bismuth and the further elements phosphor, indium and tin are added in small amounts for this purpose to the alloy.

[0013] The basic purpose of the invention is to provide an improved lead-free copper alloy with respect to its characteristics and to set forth its use.

SUMMARY OF THE INVENTION

[0014] The purpose is attained by providing a copper alloy based on copper, zinc and tin, consisting of: 60 to 70% Cu, 0.5 to 3.5% Sn and the further matrix-active elements: 0.01 to 0.5% Fe and/or Co, 0.01 to 0.5% Ni,

0.01 to 0.5% Mn and/or Si, the remainder being Zn and unavoidable impurities.

[0015] The copper alloy selectively contains, in addition, up to 3% Mg, up to 0.2% P and, selectively, each of Ag, Al, As, Sb, Ti and Zr in an amount up to 0.5%.

[0016] All parts of the alloy are disclosed in weight %.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The invention will be discussed in greater detail in connection with the drawing, in which:

[0018] Figure 1 illustrates the relationship between the standard deviations of the product characteristics and the content of matrix-active elements without majority components.

DETAILED DESCRIPTION

[0019] The invention is based on the premise that the suitable combination of the alloy elements and the characteristics resulting from cooperation of the individual parts all together meet the expectations demanded from the alloy and thus the requirement for the material should be covered. The material should for this purpose at the same time be distinguished by

- the absence of toxic elements,
- a good machining property,
- a good workability,
- a high corrosion resistance,
- an increased strength level with an equally high ductility compared to lead-containing machinable brass,
- capability for mass production in a mill for partially finished products, and
- a robust manufacture, namely, a manufacture not sensitive to fluctuating operating parameters, in a mill for partially finished products.

[0020] The copper alloy is for this purpose designed as a Sn-containing CuZn alloy (naval brass) without toxic additives. Naturally, the demands for a health-conscious and ecological compatibility are thus met.

[0021] The Cu-content of the inventive alloy lies between 60% and 70%.

[0022] Cu-contents below 60% would lead to a brittleness, which would result in a significantly low ductile yield or impact bending resistance. For example, disadvantages in the non-cutting forming would be created through this. When the Cu-content exceeds 70%, long, bulky chips would be created during an uninterrupted cut of the machining process.

[0023] Analogous situations exist regarding the Sn-content: In the case of Sn-concentrations below 0.5%, the advantage of the short chips would be lost; above 3.5% the toughness would drop off too far.

[0024] Fe or Co is necessary in order to control the grain size of the alpha phase and of the beta phase. In addition, Fe lowers the specific chip-forming operation in the alloy. The effect would not exist sufficiently below 0.01%. The risk of coarse precipitations would exist above 0.5% even together with Si. These would be disadvantageous for cold forming.

[0025] Ni, Mn and Si are used to purposefully influence the structural constitution at a given copper content. Mn and Si increase the part of the cubic-space-centered beta phase, Ni stabilizes the part of the cubic-surface-centered copper-zinc mixed crystal.

[0026] Ni below 0.01% would not be sufficient to sufficiently stabilize the copper mixed crystal, in addition, the favorable effect on the resistance to a surface-like corrosion attack would be eliminated. Ni above 0.5% would lead to an increased solidification

during cold forming and would therefore not be advantageous.

[0027] Mn below 0.01% would not be advantageous since the beta phase would then exist in amounts which would be too small. Mn above 0.5% would influence the malleability and the resistance to stress corrosion cracking.

[0028] Si below 0.01% would not be advantageous since the amount of beta phase would be too low, Si above 0.5% would influence the cold-forming ability.

[0029] Mg reduces the specific chip-forming operation in alloys and contributes significantly to the improvement of the machinability property. The cause lies in the formation of low-melting eutectic phase parts in the binary bounding system Cu-Mg and Zn-Mg. The eutectic composition is brittle and thus represents a predetermined breaking point in the structure where chip breaking can be started. The toughness would drop off too far above 3% and manufacture via continuous casting would no longer be possible.

[0030] P is selectively provided in order to favorably influence the formation of the initial cast structure and the corrosion characteristics. Phosphor increases the flowing ability of the melt and acts favorably against the susceptibility of stress corrosion cracking. In addition, P acts against the elutriation of zinc from brass. In particular, starting with an amount of 0.003%, these effects are significant. Above 0.2%, however, the disadvantages would be predominant due to an increased tendency for intercrystalline corrosion at grain boundaries.

[0031] It is optional to add up to 0.5% aluminum by alloying in order to enable the creation of starting layers. This is particularly advantageous for decorative purposes. This effect is particularly significant

starting with an amount of 0.003%. Amounts above 0.5% would no longer be advantageous for this use because the formation of a beta phase would be favored.

[0032] Partially finished products made out of the inventive material are preferably manufactured by conventional continuous casting, extrusion at temperatures of between 600°C to 750°C and a cold forming, for example by drawing.

[0033] The composition has proven to be able to be manufactured without any problems and has proven to be surprisingly constant in its characteristics in this manufacturing sequence. This is not the case with ternary alloys of Cu-Zn-Sn, as they are commonly discussed in literature. They lack the favorable characteristics in continuous casting and a stable structure formation, which depends little on the variations of the operating parameters, for example during extrusion. This is true for both the steady course of the technological characteristic values in the finished product itself, and also for the unchanged characteristics between various processed cast charges. It appears that the extent of variations of the finished round bars depends in its characteristics in the first approximation of the content of the matrix-active elements. On the basis of the majority components Cu, Zn and Sn, there is the content in the sum of the matrix-active elements Fe, Co, Ni, Mn and Si, which are at least partially soluble in the matrix, alone or in combination with the selective elements Mg, P, Ag, Al, As, Sb, Ti and Zr, obviously of a significant importance for the robust manufacture in the mill for partially finished products, which manufacture is insensitive with respect to fluctuating operating parameters.

[0034] The copper alloy consists, in a preferred embodiment, of 60 to 70% Cu, 0.5 to 3.5% Sn, 0.07 to 3%

Mg and 0.003 to 0.01% P, the remainder being Zn and unavoidable impurities.

[0035] The copper alloy consists alternatively and in a further preferred embodiment of 60 to 70% Cu, 0.5 to 3.5% Sn, 0.07 to 3% Mg and 0.03 to 0.1% P, the remainder being Zn and unavoidable impurities.

[0036] The copper alloy consist alternatively and in a further preferred embodiment of 60 to 70% Cu, 1.5 to 2.5% Sn, 0.07 to 3% Mg and 0.03 to 0.1% P, the remainder being Zn and unavoidable impurities.

[0037] The copper alloy consists alternatively and in a further preferred embodiment of 60 to 70% Cu, 2.0 to 2.5% Sn, 0.07 to 3% Mg and 0.03 to 0.1% P, the remainder being Zn and unavoidable impurities.

[0038] All of the above-mentioned preferred embodiments contain phosphor in order to, in particular, favorably influence the creation of the initial cast structure and the corrosion characteristics. These alloy compositions with an amount of 0.03 to 0.1% P meet, in a particularly favorable manner, the expectations placed on the material.

[0039] It appears that with the contents of the matrix-active elements,other than Cu, Zn and Sn, below a certain amount, such large dispersions of technological characteristics occur that this has a lasting effect on the manufacture and, in the extreme case, a safe control of the production process is not possible. In order to counteract this, 0.5 to 5% of the total content of the further matrix-active and the selectively added elements is advantageously in the copper alloy.

[0040] The dispersion is already clearly reduced at these amounts and finds its optimum in many standard processes in a particularly preferred embodiment with a total content of between 0.7 to 1%.

[0041] Depending on the process it can, however, also be sensible to instead supply a high amount of matrix-active elements. The practicability exists, however, only up to a total content of 5% at a maximum. However, no practically meaningful improvements of the dispersions can be observed beyond contents of 5% since considerable unpredictable superposed additive effects are noticed, which ruin the intended purpose.

[0042] The copper alloy is advantageously utilized for contacts, pins or fastening elements in electrical engineering, for example as stationary contacts or solid-state contacts, part of which are also clamping joints and plug connectors or connector contacts, and also in the telecommunication technology.

[0043] The alloy has, when used with liquidy and gaseous media, a high corrosion resistance. In addition, it is extremely resistant to dezincing and stress corrosion cracking. Consequently, the alloy is advantageously suited for use in containers for the transport or storage of liquids or gases, in particular, containers in the field of refrigeration technology or for tubes, water fittings, faucet extensions, pipe joints and valves in the field of sanitation technology.

[0044] The insensitivity with respect to stress corrosion cracking suggests the use of the alloy in screw connections or clamping joints, where, technically caused, high elastic energies are stored. Thus, particularly advantageous is the use of the alloy for all tensile-stressed and/or torsion-stressed components, in particular for screws and nuts. The inventive material reaches, after cold forming, higher values for the yield strength than Pb-containing CuZn alloys. Thus, it is possible to realize in screw connections, which may not plastically deform, greater tightening torques. The apparent yielding point ratio $R_{p0.2}/R_m$ is smaller for the

CuZnSn alloy than in free-cutting brass. Screw connections, which are only tightened once and are thereby intentionally overstressed, achieve with this particularly high retention forces. Because of the higher strength level, savings in weight of at least 10% are possible through a miniaturization.

[0045] The low corrosion rates guarantee also that the negligence regarding the metal, that is, the characteristic of removing through the action of liquidy or gaseous media alloy parts, is actually low. In this respect, the material is suited for areas of use which demand a low emission of contaminants in order to protect the environment. Thus, the use of the inventive alloy lies advantageously in the field of recyclable components.

[0046] The inventive alloy shows a distinctive temperature dependency of the impact tenacity. The impact tenacity drops at temperatures of above 600°C to values which correspond to those of some Pb-containing alloys and promise an advantageous use for die-formed parts.

[0047] The inventive alloy has, even without lead as an alloy part, a good cutting property. It thus is also suited for the manufacture of slide elements for the car industry and the air-travel and space-travel technologies.

[0048] Possibilities for use of the copper alloy are both for tube-shaped and also strip-shaped starting materials. Advantageously, easily millable or punchable strips, sheet metal and plates are suited in particular for keys, engravings, decorative purposes or for pressed-screen applications. For manufacture, a conventional continuous casting is preferred, hot rolling between 500 to 850°C with a subsequent forming, as for example cold rolling and, if needed, supplemented by further annealing

and forming steps, to form suitable partially finished strip products. The alloy can be utilized as a malleable, rolling or casting alloy.

[0049] The advantages achieved with the invention consists, in particular, in these having a good cutting property and good forming ability in connection with a high corrosion resistance. The resistance to dezincing and stress corrosion cracking is hereby especially distinctive.

[0050] In addition, toxic elements are absent which, due to increasingly stricter standards for protecting the environment, enable a free use, in particular, in connection with drinking-water systems.

[0051] A further important advantage is an increased strength level with an equally high ductility compared to lead-containing machinable brass.

[0052] Narrow manufacturing tolerances play an important role in the manufacture of the alloy. Particularly advantageous in the inventive alloy is its suitability for mass production in a mill for partially finished products with respect to a robust manufacture, namely a manufacture insensitive to fluctuating operating parameters.

[0053] Figure 1 illustrates the relationship between the standard deviation of the product characteristics and the content of matrix-active elements without majority components. The curve shows the to be expected trend for the standard deviation without consideration of further effects. Thus, it appears that in the case of the contents of the matrix-active elements, except for Cu, Zn and Sn, the dispersions of the technological characteristics decrease asymptotically over a certain part, from which the conclusion results that an as high as possible part of the matrix-active elements is to be supplied. However, practice shows that the desired

material characteristics occur only up to a total content of 5% at a maximum. Above contents of 5%, no further improvements of the dispersions can be observed since considerable unpredictable superposed additive effects are observed, which do not lead to any further improvement.

[0054] The variability of the material characteristics which, through use of the inventive composition, move particularly into the foreground, are the apparent yielding point, the tensile strength, the ductile yield, the hardness, the grain size and the hardening ability of the material. During the further course of the processing through cold forming and annealing, if desired, corresponding observations are made.

[0055] Tests on Mg-containing alloys have shown that after a forming operation by extrusion at 690°C, the eutectic phase parts are formed into the structure as brittle precipitations. This change in the structure can be further reinforced through a heat after-treatment at 500°C. The partially finished products receive their final form and strength by a cold forming through drawing.